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PATENT APPLICATION

METHODS AND FORMULATIONS FOR PROVIDING GLOSS COATINGS TO FOODS AND FOR PROTECTING NUTS FROM RANCIDITY

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METHODS AND FORMULATIONS FOR PROVIDING GLOSS COATINGS TO FOODS AND FOR PROTECTING NUTS FROM RANCIDITY

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application is related to co-pending U.S. patent application 09/879,796, filed June 11, 2001.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

Not applicable.

BACKGROUND OF THE INVENTION

[0002] Glazing is usually done as the final step in making high quality confectioneries, to provide a brilliant surface and a moisture-barrier coating. Glazing is generally achieved using edible wax and/or shellac (Bertram, H.T., *The Manufacturing Confectioner*, **68**(10):65-69 (1988). Shellac coating, in addition to giving a brilliant finish, provides very good protection against high humidity (Minifie, B.W., *Chocolate, Cocoa & Confectionery: Science & Technology*, 2nd Ed., AVI Publishing Company, Inc ., Westport, Connecticut, pp. 105-127 (1980a). Shellac is a resinous secretion of the lac beetle and is refined to be used for the preparation of varnishes and polishes (Minifie, B.W., *Science & Technology*, 2nd Ed., AVI Publishing Company, Inc., Westport, Connecticut, p 252-273 (1980b). Prior to the glazing step, a gum solution is applied to seal the pores and cracks of the chocolate surface (Bertram, H.T., *The Manufacturing Confectioner*, **68**(10):65-69 (1988); Strub, R., *The Manufacturing Confectioner*, 51-54 (1987). The main reason for the gum coating is to provide a barrier to the possible absorption of ethanol from the shellac coating solution into the chocolate. Ethanol, which is miscible with the fats and oils contained in chocolate, may cause bitter and off-flavors which are not desirable (Isganitis, D.K., *The Manufacturing Confectioner*, **68**(10):75-78 (1988).

[0003] Using ethanol as solvent can also produce volatile organic compounds which are hazardous to the environment. Ethanol-based shellac also possesses a potential explosion

hazard during processing (Minifie, B.W., *Chocolate, Cocoa & Confectionery: Science & Technology*, 2nd Ed., AVI Publishing Company, Inc., Westport, Connecticut, pp. 105-127 (1980a). A water-based glaze formulation would not only be able to eliminate one processing step (gum coating step), but it would also eliminate the potential explosion and environmental hazards. Additionally, many consumers would find elimination of an insect-based coating to be more palatable than an insect-based coating.

[0004] Whey proteins with plasticizer form transparent and flexible films when cast and dried from aqueous solution. A whey protein film using glycerol as a plasticizer was shown to provide high gloss, comparable to shellac, dextrin and corn zein and better than HPMC coatings, when coated on matte black acrylic plastic (Trezza, et al., *J. Food Sci.*, **65**(4): 658-662 (2000) (hereafter, "Trezza 2000")). Unfortunately, when applied to chocolate rather than plastic, the whey protein-based film described in Trezza 2000 had a lower initial gloss value than it had had on plastic, and a rapid rate of gloss fade that resulted in the loss of gloss within a few days. It would be useful to have gloss coatings for confections and other foods that provide a higher gloss value and a gloss stable enough for use in normal commercial applications.

[0005] Another aspect of food acceptance by consumers is the freshness of peanuts and other nuts (although peanuts are technically legumes, they are considered as nuts in the mind of the public and are, for example, the predominant component of most so-called "mixed nut" products). Peanuts and other nuts are high in oil and fat content. In peanuts, for example, these oils and fats mainly consist of unsaturated fatty acid providing high vulnerability to oxidative rancidity (Conkerton and St. Angelo, Peanuts (Groundnuts), In: Wolff IA, editors, *CRC Handbook of Processing and Utilization in Agriculture*, Vol. 2, Part 2, Plant Products. Boca Raton, Florida. CRC Press, p 157- (1983); Yuki et al., *J. Jpn. Soc. Food Sci. Technol.*, 25:293-301 (1978); Ahmed and Young, Composition, quality, and flavor of peanuts. *In: Peanut Science and Technology*, Amer. Peanut Res. & Educ. Assoc., Yoakum, Texas, p. 655-688). For roasted peanuts, autoxidation is the major cause of oxidative rancidity (Divino et al., *J. Food Sci.*, 61(1):112-115, 120 (1996)). Autoxidation in peanuts results in 'flavor-fade' and off-flavor development, due to the masking of pyrazines by large amounts of low-molecular weight aldehydes such as hexanal (Warner et al., *J. Food Sci.*, 61(2):469-472 (1996); Dimick, PS, Peanut flavor-fade research report, The manufacturing confectioner, Jan.: 45-48 (1994)). Hexanal, which is a major breakdown product of the linoleic acid oxidation (Frankel EN, *Prog. Lipid Res.*, 22:1-33 (1982)), has been shown to be a good

indicator of oxidative rancidity in peanuts (Maté et al., *J. Agric. Food Chem.*, 44:1736-1740 (1996).

[0006] Whey-protein-isolate ("WPI")-based films using heat denatured WPI have been found to be oxygen barriers (Maté and Krochta, *J. Agric. Food Chem.*, 44(10):3001-3004 (1996)). Whey protein coatings applied by a bench-scale coating method have been shown to provide some protection against oxidative rancidity in peanuts when analyzed by chemical and instrumental methods (Maté and Krochta, *J. Food Sci.*, 61(6):1202-1206, 1210 (1996); Maté et al., *J. Agric. Food Chem.*, 44:1736-1740 (1996)). Application of whey protein films to peanuts, however, required viscous films, and achieving that viscosity required the whey protein mixture to sit for several days. It would be desirable to find improved methods for creating whey protein films that did not require materials to be prepared for days in advance of use.

BRIEF SUMMARY OF THE INVENTION

[0007] The invention provides new methods and formulations for providing gloss coatings to foods.

[0008] In one important set of embodiments, the invention provides gloss coatings for foods wherein the coating comprises whey protein concentrate (WPC), hydrolyzed whey protein, soy protein concentrate (SPC), beta-lactoglobulin, alpha-lactalbumin, milk casein, egg white protein, wheat gluten, cottonseed protein, peanut protein, rice protein, or pea protein, or a combination thereof, and a food grade plasticizer. The food grade plasticizer can be a mono-, di-, tri, oligo- or poly- saccharide or a polyhydric alcohol that is a solid at room temperature. In some embodiments, the coating comprises WPC. In some embodiments, the plasticizer is a disaccharide. In particular embodiments, the plasticizer is sucrose, maltose, trehalose, cellobiose, or lactose, and is preferably sucrose. In some preferred embodiments, the food is a confection, particularly chocolate. The chocolate can be, for example, milk chocolate, semi-sweet chocolate, bitter-sweet chocolate, sweet chocolate, dark chocolate, or imitation chocolate. The confection can be, for example, a hard panned confection, a soft panned confection, a starch molded confection and a compressed sugar tablet. The confection can have an exterior surface comprising a dried yogurt formulation. The gloss coating can comprise WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin that is denatured. Alternatively, it can comprise WPC,

hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin that has not been denatured, or it can comprise both denatured and non-denatured WPC or SPC, or both denatured and non-denatured WPC and SPC. The coating may further comprise whey protein isolate, soy protein isolate, or both, and may further comprise a lipid. In some embodiments, the lipid is cocoabutter.

[0009] In another important group of embodiments, the invention provides gloss coatings for food, wherein the coating comprises (a) whey protein isolate (WPI), whey protein concentrate (WPC), hydrolyzed whey protein, soy protein isolate (SPI), soy protein concentrate (SPC), beta-lactoglobulin, alpha-lactalbumin, milk casein, egg white protein, wheat gluten, cottonseed protein, peanut protein, rice protein, or pea protein, (b) a first food grade plasticizer selected from the group consisting of a mono-, di-, tri, oligo- or poly-saccharide and a polyhydric alcohol that is a solid at room temperature, and (c) a second food grade plasticizer selected from the group consisting of a mono-, di-, tri, oligo- or poly-saccharide and a polyhydric alcohol that is a solid at room temperature, provided that the second food grade plasticizer is not the same as the first food grade plasticizer. In some embodiments, the first food grade plasticizer is a disaccharide. In some embodiments, the disaccharide is sucrose, maltose, trehalose, cellobiose or lactose. The food may be a confection. In some embodiments, the confection is chocolate. In some embodiments, the chocolate is milk chocolate, semi-sweet chocolate, bitter-sweet chocolate, sweet chocolate, dark chocolate, or imitation chocolate. The confection may be a hard panned confection, a soft panned confection, a starch molded confection or a compressed sugar tablet. It may have an exterior surface comprising a dried yogurt formulation. The coating may comprise WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin that is denatured. In some embodiments, the coating may contain WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin that has not been denatured. In some embodiments, it may contain both denatured and non-denatured WPI, SPI, or both denatured and non-denatured WPI and SPI. The coating may further comprise a lipid. In some embodiments, the lipid is cocoabutter.

[0010] In yet another important group of embodiments, the invention provides methods of providing an edible gloss coating to a food. In some embodiments, the method comprises coating the food with (a) a film-forming protein selected from the group consisting of whey protein concentrate (WPC), hydrolyzed whey protein, soy protein concentrate (SPC), beta-lactoglobulin, alpha-lactalbumin, milk casein, egg white protein, wheat gluten, cottonseed

protein, peanut protein, rice protein or pea protein and (b) a food grade plasticizer selected from the group consisting of (i) a mono-, di-, tri, oligo- or poly- saccharide and (ii) a polyhydric alcohol that is a solid at room temperature. In some embodiments, the film-forming protein is WPC. In some embodiments, the food grade plasticizer is a disaccharide. The disaccharide may be sucrose, maltose, trehalose, cellobiose, or lactose. The food may be a confection. In some embodiments, the confection is chocolate. In some embodiments, the chocolate is milk chocolate, semi-sweet chocolate, bitter-sweet chocolate, sweet chocolate, dark chocolate, or imitation chocolate. The confection may be a hard panned confection, a soft panned confection, a starch molded confection or a compressed sugar tablet. It may have an exterior surface comprising a dried yogurt formulation. In some embodiments, the WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin is denatured. In some embodiments, the WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin is not denatured. In some embodiments, the coating comprises denatured and non-denatured WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin, or a combination thereof.

[0011] In still another important group of embodiments, the invention provides methods of providing an edible gloss coating to a food, comprising contacting the food with (a) a film-forming protein selected from the group consisting of whey protein isolate (WPI) whey protein concentrate (WPC), hydrolyzed whey protein, soy protein isolate (SPI), soy protein concentrate (SPC), beta-lactoglobulin, alpha-lactalbumin, milk casein, egg white protein, wheat gluten, cottonseed protein, peanut protein, rice protein and pea protein, (b) a first food grade plasticizer selected from the group consisting of (i) a mono-, di-, tri, oligo- or poly-saccharide and (ii) a polyhydric alcohol that is a solid at room temperature and, (c) a second food grade plasticizer selected from the group consisting of (i) a mono-, di-, tri, oligo- or poly- saccharide and (ii) a polyhydric alcohol that is a solid at room temperature, provided that the second food grade plasticizer is not the same as the first food grade plasticizer. In some embodiments, the film-forming protein is WPI. In some embodiments, the first food grade plasticizer is a disaccharide, and is preferably sucrose. The food may be a confection. In some embodiments, the confection is chocolate. In some embodiments, the chocolate is milk chocolate, semi-sweet chocolate, bitter-sweet chocolate, sweet chocolate, dark chocolate, or imitation chocolate. The confection may be a hard panned confection, a soft panned confection, a starch molded confection or a compressed sugar tablet. It may have an exterior surface comprising a dried yogurt formulation. In some embodiments, the WPI, SPI,

WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin is denatured. In some embodiments, the WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin is not denatured. In some embodiments, the coating comprises a mixture of denatured and non-denatured WPI or SPI, or of both. In some embodiments, the coating comprises two or more film-forming proteins selected from the group consisting of whey protein isolate (WPI) whey protein concentrate (WPC), hydrolyzed whey protein, soy protein isolate (SPI), soy protein concentrate (SPC), beta-lactoglobulin, alpha-lactalbumin, milk casein, egg white protein, wheat gluten, cottonseed protein, peanut protein, rice protein and pea protein.

[0012] The invention further provides methods for increasing shelf life of a nut. The method comprises contacting said nut with an aqueous solution comprising (a) a film-forming agent selected from the group consisting of whey protein isolate (WPI), soy protein isolate (SPI), whey protein concentrate (WPC), hydrolyzed whey protein, soy protein concentrate (SPC), beta-lactoglobulin, alpha-lactalbumin, milk casein, egg white protein, wheat gluten, cottonseed protein, peanut protein, rice protein and pea protein agent, and (b) a food grade surfactant, wherein said food grade surfactant is present in said solution in an amount greater than an amount which lowers the surface energy of the solution to its lowest value, thereby increasing its shelf life. In some embodiments, the surfactant is lecithin. The solution may further comprise a plasticizer. The WPI, SPI, WPC, hydrolyzed whey protein, SPC, beta-lactoglobulin, or alpha-lactalbumin can be denatured, or non-denatured, or a combination of denatured and non-denatured protein or proteins. The nut may optionally be roughened by mild abrasion prior to or currently with contacting said nut with said aqueous solution. The nut can be a peanut, an almond, cashew, walnut, hazelnut, pecan, macadamia, pistachio, or Brazil nut.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The invention provides new methods of providing more stable gloss coatings to foods, such as chocolates and other confections, and to protecting peanuts and nuts from rancidity. The present invention provides new materials for forming such coatings, additional plasticizers for the materials, new methods for inhibiting crystallization of the plasticizers, thereby extending the shelf life of the gloss coating, and new methods for improving the efficiency of coverage and adhesion of oxygen-barrier coatings on nuts, thereby extending the shelf life of these products before unacceptable rancidity.

A. Gloss coatings for foods

[0014] In one set of embodiments, the invention provides stable, water-based gloss coatings for foods, such as chocolates and other confections, on which gloss coatings are desirable. As discussed in the Background section, current formulations for providing gloss coatings or glazings to chocolates and other confections typically require the use of volatile organic compunds (VOCs) such as ethanol. As discussed above, in Trezza 2000, the researchers disclosed a possible alternative involving a water-based formulation. The results on standard plastic casting plates used to measure gloss indicated that an edible film using whey protein and glycerol as a plasticizer would give a gloss comparable to that of shellac. Unfortunately, when actually tested on chocolate, glycerol-plasticized coating proved to have a relatively low gloss value and a rapid rate of gloss fade. Within days of coating, the gloss faded away, and the coating had a low residual gloss value. Thus, the results on plastic plates were not predictive of results on chocolate.

1. WPI films for edible coatings

[0015] Co-owned U.S. patent application 09/879,796, filed June 11, 2001, discloses that edible film coatings could be made from whey protein isolate ("WPI") or soy protein isolate ("SPI"), using sucrose or other disaccharides, such as maltose or lactose, as a plasticizer. It was known in the art that sucrose could be used as a plasticizer. It was also known, however, that plasticizers that are solid at room temperature, such as sucrose, tend to crystallize rapidly. Films using solid plasticizers therefore tend to become marred by crystal formation, resulting in an undesirable lumpy, milky appearance rather than an even gloss. The art has therefore generally avoided solid plasticizers in favor of liquid plasticizers, with glycerol being the plasticizer most commonly used.

[0016] The '796 application discloses that, for use on foods, and especially on confections, native (undenatured) WPI-, and SPI- based films made with sucrose or other disaccharide plasticizers had surprising advantages for use on foods that do not have a peel or other barrier to migration of components of the film. The application indicates that such films provide a gloss that has a high initial gloss value, and that the films stabilize at a high gloss value and retain that gloss value over a period of one month, two months, or even longer. The application states that sucrose and other disaccharides are surprisingly superior plasticizers for edible films for use on confections.

2. Whey protein concentrates vs. whey protein isolates

[0017] Until relatively recently, whey protein was considered a waste product of cheese production, and was used as animal feed or discarded. More recently, whey protein concentrate has seen use as a nutritional supplement touted as a complete protein for body builders and athletes. Typically, the raw whey, resulting from the precipitation of casein and milkfat from milk in cheesemaking, is filtered or centrifuged to remove any remaining cheese particles, or "fines," passed through a centrifugal separator or ceramic membrane to remove much of the remaining fat content, and pasteurized. More recently, the whey has been placed in contact with membranes that selectively let pass some of the minerals, fat, lactose and water. The resulting product, whey protein concentrate ("WPC") varies from protein content from about 25% to 89% protein, and contains inconsistent amounts of lactose, fat and minerals. For example, 80% WPC typically might contain 80.1% protein, 7% fat, 3% ash (minerals), and 9% lactose. The WPC sold as a nutritional supplement for bodybuilders typically has a protein content of 80% to 85%. Whey protein compositions of less than 90% protein are called WPCs. WPCs with protein concentrations above 85% are commonly produced because a point of diminishing return is reached given the separation of protein that can be achieved by the technology used for WPC production.

[0018] By contrast, WPI is a highly purified substance, made in a different manner, and using more sophisticated technology than that used for production of WPC. Typically, one of two production technologies is used: the whey proteins are either adsorbed onto an ion-exchange resin, and then eluted by changing the pH, or they are subjected to pressure-driven microfiltration followed by ultrafiltration (which is sometimes followed by ion-exchange). The resulting WPI is at least 90% protein, and is more commonly at least 95% protein, with a negligible amount of fat, and 1% or less of lactose. The WPI produced by either process contains high amounts of alpha-lactalbumin, beta-lactoglobulin, bovine serum albumin and immunoglobulins.

[0019] Thus, WPC and WPI are two different products made by two different methods. Because of the differences in purifying methodologies, even WPCs with protein contents approaching those of lower grade WPIs have much higher levels of fat and lactose, and may have higher levels of ash and other components, depending on the type of cheese produced (which employ different processes for separating the whey), the season, the geographic source of the milk, the cows, and other factors.

[0020] It has been assumed that the higher levels of fat, lactose and other components would interfere with film formation. Indeed, because of the considerable variability of the levels of the various components, including fat, lactose, and minerals, as well as of protein, it was thought not only that whey protein concentrates would not make consistently good edible films, but also that, if such films could be made, that they would not provide gloss coatings stable for periods long enough to be commercially useful.

3. The formation of edible films from WPCs and component proteins

[0021] As noted in the preceding section, the levels of fat, lactose, and other components found in WPC are considerably higher than the levels of the same components in WPI, and it was thought that the variable levels of these components would interfere with the formation of consistently good edible films. Surprisingly, it has now been found that the presence and variability of these components does not interfere with the formation of consistent edible films and that the films formed with the WPC provide gloss coatings for food that are stable for one, two, or more months. The WPC used for the films can be denatured or non-denatured, and can be used by itself or in combination with denatured or native (non-denatured) WPI. Hydrolyzed whey protein can also be used. Because hydrolyzed whey protein has a somewhat bitter taste, it preferably is used as only part of the protein used for the film coating, and preferably is less than 50% of the protein used. Even more preferably, the amount used can be 40%, 30%, 25%, 20%, 15%, or 10% or less, with each successive lower amount being more preferred.

[0022] The ability to use WPC in place of WPI in gloss coatings, or to substitute WPC for some of the WPI that would otherwise be used, is advantageous. Because WPC is made using less sophisticated separation techniques, it is much less costly than WPI. Accordingly, the ability to use WPC in place of some or all of the WPI that would otherwise be needed will sharply lower the cost of gloss coatings and make them feasible in applications for which WPI-based coatings would not have been cost-effective. Moreover, by reducing the cost of the coatings even where WPI-based films would be cost-effective, the ability to use WPC-based films can encourage the conversion from ethanol-based coatings to the more environmentally friendly, water-based coatings of the invention.

[0023] Further, given the results with WPC, it is expected that the same results will obtain with soy protein concentrate ("SPC"), and that edible gloss coatings can be formed from SPC,

from a combination of SPC and SPI, or from a combination of either of these materials with WPI or WPC, or both. Indeed, it is expected that edible gloss coatings can be made from combining all four materials. SPCs are produced by removing most of the oil and water from soybeans and on a dry weight basis, typically contain more than 70% protein. Oligosaccharides and other soluble components are typically leached from the beans. In contrast, SPI typically has higher than 90% protein on a dry weight basis and have typically been prepared by isoelectric precipitation using defatted flours from which insoluble polysaccharides and other components have been extracted.

[0024] It could not be predicted from the work with protein isolates that films could be formed from component proteins. We have previously demonstrated that denatured beta lactoglobulin, a protein that is the largest single component of whey protein, forms edible films. Based on our results with native, non-denatured WPC and with denatured beta lactoglobulin, it is expected that native beta lactoglobulin can likewise be used to form edible films that maintain gloss. It is further expected that alpha lactalbumin, a second major protein component of whey protein can be separated from whey proteins and used to form edible films that have similar gloss characteristics. Numerous methods of separating these proteins from other whey proteins are known, including anion exchange, cation exchange, heat and pH treatment, ultrafiltration, chromatography, and extraction of solvents. Techniques for separating these proteins are summarized in, for example, U.S. Patent No. 5,925,737, which discloses a method for separating these fractions from whey using heat and carbon dioxide.

4. Other Proteins that Form Edible Films

[0025] While whey protein and its component proteins and soy proteins are particularly preferred for making films for use in the invention, other water-soluble proteins extractable from foods are known in the art and have been shown to be film-formers and can be used. These proteins are: milk casein (or, for greater solubility, caseinates), egg white protein, wheat gluten, cottonseed protein, peanut protein, rice protein, and pea protein. These proteins are commercially available or can be readily made. For example, casein and caseinates are available from American Casein Company (Burlington, NJ), egg white protein is available from Low Carb Nexus® (a division of Bailey Ventures, Inc., High Point, NC), wheat gluten can be made by removing the starch from wheat flour, cottonseed protein can be obtained from Xian Meheco (Xian, Shaanxi, China), rice protein is available from NutriBiotic

(Lakeport, CA) and pea protein concentrate is commercially available from Kirkman® (Lake Oswego, OR).

[0026] Individuals with celiac disease (also known as celiac sprue) are advised to avoid products made with wheat gluten, while some individuals have severe reactions to peanuts. Thus, while films can be made with these proteins, products made with these films need to be marked to alert sensitive consumers to avoid them. Thus, coatings made with other film forming proteins may be more desirable due to their potentially broader commercial market.

5. Plasticizers

[0027] As noted in part 1, above, the '796 application discloses that disaccharides such as sucrose can be used as plasticizers to form edible films that maintain gloss for a period of one, two, or more months. The application notes that, without wishing to be bound by theory, it is believed that the mass size of the molecules is a factor and that disaccharide molecules are sufficiently bulky that their movement into the confection is slowed compared to the linear molecules of glycerol, polyethylene glycol, and other commonly used plasticizers. The application noted that, in addition to sucrose, other disaccharides can be used, such as lactose, trehalose and cellobiose. Semi-sweet, sweet, and milk chocolate all contain milk solids and therefore contain at least some lactose. Thus, it was also stated that the concentration gradient of lactose in these chocolates is reduced and will tend to migrate less from coatings of those chocolates, reducing the opportunity for the gloss to fade. Since chocolates and other confections are commonly made with substantial amounts of sucrose, the sucrose in a sucrose-plasticized film also does not face a concentration gradient and thus will have a limited tendency to migrate into the confection. Thus, while any disaccharide can be used to make a satisfactory edible film to coat a food, such as a chocolate or a confection, it was stated that lactose is preferred and sucrose is the most preferred.

[0028] The '796 application further states that, in view of the results with disaccharides, it is expected that gloss coatings can also be made with monosacchrides, such as sorbitol. It noted that monosaccharides are less bulky than disaccharides, so they may be more prone to migration from the film. Accordingly, it states that disaccharides are more preferred.

[0029] In view of the results with WPI films, it is expected that disaccharides and monosaccharides can also be used as plasticizers with respect to WPC, SPC, beta lactoglobulin, and alpha lactalbumin films. It is noted however, that sorbitol is more properly

classified as a polyhydric alcohol. Given the results with sorbitol, it is expected that the polyhydric alcohols mannitol, xylitol, galactitol, malitol, and lactitol will also work as plasticizers for gloss coatings. Other polyhydric alcohols can be used, so long as they are edible and are sufficiently bulky so that they do not rapidly migrate into the food being coated. Any particular polyhydric alcohol can be readily tested for whether its migration is sufficiently slow to form useful gloss coatings following the assays taught in the Examples. As noted above, glycerol was found not to form films that maintained a stable gloss, and is not suitable for use in the methods of the invention. Without wishing to be bound by theory, it is surmised that the relatively small size of the glycerol molecule allows some migration into the food, while the larger molecules of sorbitol and other polyhydric alcohols causes them either not to migrate, or to migrate slowly enough that they permit the film to retain gloss for a commercially useful period. It should be noted that sorbitol can have a laxative effect when given in sufficient amounts. Since the invention contemplates the use of sorbitol in a limited amount in a thin film coating a food item, it is not expected that the amount of sorbitol present would be large enough to induce a laxative effect; nonetheless, other polyhydric alcohols or saccharides can be used as plasticizers if desired.

[0030] Monosaccharides suitable for use as plasticizers include glucose, fructose, galactose, and mannose. Disaccharides suitable for use in the compositions and methods of the invention include, in addition to sucrose, lactose and trehalose, lactulose, melibiose, maltose, isomaltose, cellobiose, and gentiobiose. Lactose causes gastric distress in some persons, who are considered lactose intolerant. Since the gloss coatings of the invention are contemplated to constitute a thin film over the main body of a food item, it is anticipated that the amount of lactose present in the film will be too small to cause distress. Nonetheless, if desired, the use of lactose as a plasticizer in addition to the amount already present in the WPC can be avoided.

[0031] Trisaccharides useful in the practice of the invention include raffinose, maltotriose, and manninotriose. Larger oligosaccharides suitable for use in the compositions and methods of the invention include maltose oligomers, which can be obtained from corn syrups. Polysaccharides suitable for use in the compositions and methods of the invention include hydroxypropyl methyl cellulose (HPMC), methyl cellulose (MC), hydroxypropyl cellulose (HPC), starches, modified starches, pectin, and other gums. Any particular mono-, di-, tri-, oligo-, or poly- saccharide can be readily tested for whether its migration is sufficiently slow to form useful gloss coatings following the assays taught in the Examples.

[0032] The amount of the protein to the plasticizer can range by weight from 2:1 to 1:3. The ratios are preferably 1:1 or lower; the 1:3 ratio gives the best gloss, durability and oxygen-barrier. Typically, the supplier of the WPC, SPC, or other protein source will provide a specification sheet ("spec sheet") setting forth the contents of the material. A spec sheet for WPC, for example, will typically state the lactose content. In a typical situation, a WPC might be stated to contain 85% protein and 10% lactose. Thus, the protein content will be present at a 8.5:1 ratio to the sugar, or plasticizer content, which can then be brought up to the 2:1 to 1:3 desired ratio range with the chosen plasticizer.

6. Crystallization inhibitors

[0033] As noted above, it was known in the art that sucrose could be used as a plasticizer. It was also known, however, that plasticizers that are solid at room temperature, such as sucrose, tend to crystallize. Films using solid plasticizers therefore tend to become marred by crystal formation, resulting in an undesirable lumpy, milky appearance rather than an even gloss. The art has therefore generally avoided solid plasticizers in favor of liquid plasticizers, with glycerol being the plasticizer most commonly used.

[0034] The '796 application discloses edible films that provide a gloss coating more stable than those previously achieved. Even these films, however, tend to lose some of their gloss over time. Moreover, this loss of gloss is associated with reduced capacity of the film to act as an oxygen barrier, and the consequent loss of flavor and quality of the food coated by the film. It would be desirable to have films that retain their gloss for even longer periods to improve the shelf life of the resulting products.

[0035] Surprisingly, it has now been found that a second plasticizer, such as one of the polyhydric alcohols, or mono-, di-, tri-, oligo- or poly- saccharides described in the preceding section, introduced into a formulation having another one of the polyhydric alcohols, or mono-, di-, tri-, oligo- or poly- saccharides as a plasticizer, acts as a crystallization inhibiting agent, slowing crystallization of the plasticizer, thereby extending the period during which the films retains a high gloss, and therefore its useful shelf life. (For ease of reference in this discussion, the plasticizer present in the larger amount will be referred to as the "plasticizer" and the second will be referred to as the " crystallization inhibiting agent," even though either one could be used by itself as a plasticizer.) Without wishing to be bound by theory, the inclusion of the crystallization inhibiting agent is believed to interfere with crystal nucleation

and growth of crystals of the plasticizer, presumably by disrupting the orderly arrangement of the molecules of the plasticizer. Thus, films formed with mixtures of sugars or other saccharides, or polyhydric alcohols, or both, will exhibit slower crystallization than films formed with only a single saccharide or polyhydric alcohol. This result will occur with films made with either native or denatured proteins.

[0036] This effect was not noted with regard to the films formed with WPI using sucrose as a plasticizer, presumably because lactose is present in WPI in trace amounts, typically below one percent. Thus, while the plasticizer used as a crystallization inhibition agent need not be present in large amounts, it should be present at 1% or more, and is more preferably present at 2% or more. The crystallization inhibition agent can be present at amounts that are up to roughly equal to the amount of the plasticizer. Thus, the crystallization inhibiting agent can be present in amounts ranging from 1% to 49% of that of the plasticizer. Preferably, the crystallization inhibition agent is present in amounts ranging from 3% to 30% of the plasticizer, more preferably present in amounts from 5% to about 25% of the amount of the plasticizer, still more preferably present in amounts from 7% to about 20% of the amount of the plasticizer, yet more preferably in amounts from 8% to about 15% of the amount of the plasticizer, and most preferably present at about 10% of the amount of the plasticizer.

7. Lipids

[0037] The coating or film can be made even smoother and less marked if a lipid approved for food use is added to the mixture prior to application to the chocolate or other condiment. Preferably, the lipid is one solid at room temperature. Milk fat or milk fat fractions are preferred lipids for use. Cocoa butter is more preferred and is especially preferred for use in coatings for chocolates since it is already in the chocolate (except, of course, in imitation chocolates). It will therefore have a reduced concentration gradient and consequently a reduced possibility of migration out of the film into the chocolate.

8. Coatings Mixing Denatured and Non-denatured Proteins

[0038] Methods of making water-insoluble films and coatings from water based WPI solutions are known. See, Krochta, U.S. Patent No. 5,543,164. These methods use denaturing of the proteins with heat, chemicals and/or enzymes to induce thiol-disulfide interchange and thiol oxidation reactions, thereby forming new intermolecular and intramolecular disulfide crosslinkages. Coatings made with denatured proteins can be used in the compositions and methods of the present invention to protect the condiment from

moisture. Mixtures of various proportions of denatured and non-denatured proteins can be used to impart any desired level of protection from moisture. For example, if moisture protection is not important for the product of interest, native (undenatured) WPI or WPC can be used and the step of denaturing the WPI or WPC avoided. If it is important, however, the WPI or WPC can be denatured to add a level of moisture protection to the condiment.

[0039] It is understood that the solution could contain SPI or SPC, beta-lactoglobulin or alpha-lactalbumin, or combinations of any of these. The combination of these film-forming proteins can be denatured or native, such as denatured SPI with non-denatured WPC and denatured hydrolyzed whey protein or non-denatured WPI with denatured WPI and non-denatured WPC.

[0040] Solutions containing native (undenatured) WPI or WPC or composed only of native WPI or WPC are also advantageous because higher amounts of solids can be introduced into the mixture, reducing the amount of water that has to be evaporated to leave the film coating the food article. WPI cannot be denatured in water at concentrations above about 12% by weight for film production without undesirable gelling. By contrast, native WPI or WPC can be dissolved at levels up to about 40% by weight. And, these concentrations are additive, so that solutions of about 12% by weight of denatured WPI to which 40% by weight of native WPI, WPC, or hydrolyzed whey protein are added can be made. Since higher concentrations reduce the amount of water to be evaporated, the time to form the films or coatings on food articles can be reduced.

8. Preferred Uses

[0041] The compositions and method of the invention are useful as coatings for foods, and particularly for confections. In preferred forms, the coatings and methods of the invention can be used to provide gloss coatings for yogurt-coated confections such as raisins and pretzels. Similarly, the coatings and methods of the invention can be used on starch molded confections, such as gummy products (such as "gummy bears") and on soft panned confections, such as jelly beans and related products. The invention can also be used on hard panned confections, that have a hard sugar coating, such as "jaw breakers" and M&Ms®, and mints, as well as on compressed sugar tablets. The coatings of the invention are particularly suitable for use with confections that do not have to be baked or cooked after application of the edible film or coating.

[0042] In a particularly preferred group of embodiments, the confections comprise chocolate as the exterior surface of the confection. Thus, the coatings can be used not only

for chocolate bars and chocolate sold by the piece (including confections having a filling surrounded by chocolate), but also for the familiar candy bar, in which a wafer, caramel, peanut mix, or other sweet is covered with chocolate.

[0043] In preferred embodiments, the food or confection uses sucrose as a sweetening agent. The coatings and methods of the invention can be used with artificially sweetened condiments, but in such confections there is a greater concentration gradient between the coating and the confection or other food itself and the gloss may therefore stabilize at a lower level than is true with sugar-sweetened foods or confections. Whether the coating stabilizes at a level that is satisfactory for any particular food or confection can be readily determined using the assays for measuring gloss and for measuring consumer acceptance set forth in the Examples.

B. Coatings for Delaying Rancidity in Nuts

[0044] In another set of embodiments, the invention provides new ways of delaying the development of rancidity in peanuts and nuts. Although peanuts are legumes, they are commonly considered nuts by the public and included in sales of mixed "nuts." Accordingly, as used herein, the terms "nut" and "nuts" include peanuts unless otherwise specified or required by context.

[0045] In earlier work, WPI films were used to delay rancidity in nuts. One problem in applying these aqueous-based films to nuts and peanuts resulted from the high oil content typically found in nuts. Water tends to "bead" on nuts. Attempts to coat the nuts with WPI films by dipping them in a solution containing a surfactant proved insufficient to coat the nuts. To overcome the hydrophobicity of the nuts, the WPI compositions were "aged" for several days under refrigeration to increase their viscosity, thereby increasing their ability to adhere to the nut long enough to coat it.

[0046] The '796 application discloses that the several days needed to age of the WPI solution can be eliminated by mildly abrading the nuts. Surprisingly, the addition of mild abrasion, such as mechanical agitation, removed the need to "age" the formulations to increase viscosity.

[0047] Surprisingly, the present invention provides a different solution to the problem of applying aqueous-based films to nuts. The invention involves a new method of applying surfactants to the nuts.

[0048] A food grade surfactant is typically added to aid spreading of the coating solution (i.e., to prevent "beading") and adhesion of the film-forming agent. Surfactant molecules include a portion that is hydrophobic and a portion that is hydrophilic. The surfaces of nuts are hydrophobic, and typically have low surface energy. For example, the surface energy of a peanut is approximately 37 dynes/cm. The aqueous coating formulations are hydrophilic, and have a higher surface energy, typically about 50 dynes/cm, than the surface of the nuts to which it is desired to apply them. Persons of skill will appreciate that coating formulations spread more readily on a surface if the surface energy of the coating formulation is slightly below the surface energy of the surface to be coated. The rule of thumb is for the surface energy of the coating solution to be at least 10 dynes/cm lower than the surface energy of the surface to be coated. Desirably, the addition of a surfactant, therefore, would lower the surface energy of the coating formulation to at least 10 dynes/cm below that of the surface to be covered. When surfactants were added to protein film coating formulations at levels which gave the lowest surface energy possible with that surfactant in that coating formulation, however, it did not result in formulations having surface energies sufficiently below those of the nuts to be coated to permit ready spreading of the coating over the nut surface. Thus, the long chilling and coating process, or abrasion processes described above were developed.

[0049] Surprisingly, it has now been discovered that adding surfactants in amounts higher than those which result in the lowest surface energy for the surfactant-protein coating formulation causes an increase in the surface energy of the nut surface, leading to more complete spreading of the coating formulation, greater coverage of the nut surface and improved adhesion of the resulting coating. The surface energy of the nut surface can be increased to as much as approximately 70 dynes/cm, which is well above that of the surfactant-protein coating mixture. This increase in the surface energy of the nut surface results in the nut surface having a higher surface energy than that of the protein coating-surfactant mixture, enhancing the coverage and adhesion of the mixture to the nut surface. The adhesion of the coating to the surface of the nut can further be improved by roughening the surface of the nut by abrasion before or during the application of the coating.

[0050] Suitable surfactants for use in the methods of the invention are ethoxylates such as TWEEN and sorbitan esters such as Span™. Lecithin, TWEEN 85, and Span™ 20 are exemplar food grade surfactants. The compositions may further comprise a plasticizer.

[0051] If abrasion is used to roughen the nut surface, desirably, it is not so great as to damage the nut or to reduce the attractiveness of its appearance. Conveniently, the abrasion can be provided by rolling the nut in a container (for example, by rotating or by vibrating the container) or by contacting the nut with other nuts, either of the same type or of other types, and then causing them to move relative to one another. This can be caused by any convenient means, such as by placing the nut or nuts in a container and then jostling, shaking, vibrating or rotating the container prior to or concurrently with contacting the nuts with the coating formulation.

[0052] Alternatively, the nuts can be placed in a container with the formulations and mechanical action or agitation added to move the nuts in the container and bring them into contact with one another. For example, the nuts can be stirred with a stirring rod or a mechanical agitator. In a preferred embodiment, the nuts and the formulation are placed in a confectionery "pan" (a stainless steel drum which resembles a cement mixer) and the drum of the pan rotated. Nuts with a round or oval configuration are easily contacted with the solution in this way for 20 seconds up to several minutes. Nuts with shapes which make it harder to contact the entire surface easily (such as cashew, which have an interior curve which is a little less accessible, or nuts with grooves or other indentations which are harder to reach, such as walnuts) should be subjected to the agitation for a longer period, preferably from a minute to several minutes, to facilitate more even contacting with the solution. It is anticipated that the contacting will still retard overall degradation of the nut even if less than 100% of the surface is subjected to abrasion.

[0053] Once the nut has been contacted with the formulation, it is desirably dried to its original water content. The particular method of drying the nuts is not critical. For example, the nuts can be air dried, room air can be blown on them, heated air can be blown on them, or the nuts can be passaged through a tunnel drier, and the time can be as much as necessary to return to their original water content.

[0054] Regarding determining the development of rancidity, it can be noted that, following exposure to air, nuts undergo a so-called induction period. The end of the induction period is denoted by a marked increase in production of oxidation products of oils present in the nut. This period until the end of the induction period can conveniently be considered as the shelf life of the nut. While shelf life can be determined by any convenient means, food scientists often use a particular degradation product, hexanal, as a marker for oxidation of nut oils. Hexanal, which is a major breakdown product of the linoleic acid oxidation (Frankel EN, *Prog. Lipid Res.*, 22:1-33 (1982)), has been shown to be a good indicator of oxidative

rancidity in peanuts (Maté et al., *J. Agric. Food Chem.*, 44:1736-1740 (1996)). Volatiles such as hexanal can be detected by various assay formats known in the art. In a preferred embodiment, the assay format is static headspace gas chromatography. Samples of the nut under study are taken at various points in time and ground to a powder to provide increased surface area and thereby release any volatile degradation products. Volatile degradation products for other nuts are known in the art. If the nut of interest is one other than peanut, the assay can be used to detect the presence of a volatile degradation product known to be produced by the nut of interest.

[0055] The invention is particularly useful with regard to peanuts. As noted above, although scientifically the peanut is classified as a legume, in the mind of the public, it is considered a nut. Indeed, commercially sold containers of "mixed nuts" typically contain peanuts as the predominant "nut" present. Studies on peanuts have shown that contacting a peanut with water and then drying it results in a marked extension of shelf life. Without wishing to be bound by theory, it is believed that the surface of the peanut has pores that permit air access below the surface of the peanut and that the presence of water causes the surface around the pores to expand, collapsing the pores, thereby rendering the surface of the nut less permeable to air. References below to nuts include peanuts unless otherwise specified. The invention is applicable to all types of nuts, such as pecans, almonds, cashews, walnuts, Brazil nuts, macadamia nuts, and hazel nuts.

Definitions

[0056] Unless otherwise defined, terms used herein have their ordinary meaning as used in the art.

[0057] As used herein, the terms "plasticizer" and "food grade plasticizer" refer to compounds which increase the flexibility of films and which have been approved for use in foods. Preferred plasticizers are disaccharides, with sucrose being the most preferred. Solid polyalcohols such as sorbitol may be used.

[0058] As used herein, "food grade" means approved for human consumption by any necessary authorities. Unless otherwise specified, all plasticizers, surfactants, lipids, whey proteins, soy proteins, and other components of the films and coatings discussed herein are assumed to be of food grade.

[0059] As used herein, the term "film" refers to a stand-alone thin layer of material which is flexible and which can be used as a wrapping. Films of the present invention are formed either with a protein or a protein in combination with a plasticizer and may further comprise a

lipid. Additionally, films may be formed from emulsified mixtures containing proteins and lipids.

[0060] As used herein, the term "coating" refers to a thin film, which surrounds the coated object. Coatings will not typically have the mechanical strength to exist as stand-alone films and are formed by applying a diluted component mixture to an object and evaporating excess solvent.

[0061] As used herein, "chocolate" refers to a confection in which one or more surfaces are formed of exposed chocolate on which a gloss coat would be desirable, in contrast to candies such as "M&Ms," in which the chocolate is fully concealed by a hard candy shell. Preferably, the chocolate is one intended for eating as a confection, in distinction to "baking" or "bitter" chocolate, which is generally intended for baking. Thus, milk chocolate, sweet chocolate, dark chocolate, and semi-sweet or bitter- sweet chocolate are all encompassed in the chocolates, which can be used in the invention. Compositions of the various kinds of chocolates are known in the art, and set forth in standard works, such as H. W. Ockerman, Source Book for Food Scientists (Avi Publishing, Westport, CT 1978). The term also refers to so-called "imitation chocolate" in which the cocoa fat in the chocolate liquor is replaced with another vegetable fat. Such imitation chocolates are used for coating ice cream bars, crackers or candies and the substitution of the cocoa butter can improve resistance to melting or other properties. See, e.g., Potter and Hotchkiss, Food Science, 5th Ed. 1995 (Chapman and Hall, NY).

[0062] As used herein, the term "lipid" refers to food grade oils, waxes, fatty acids, fatty alcohols, monoglycerides and triglycerides having long carbon chains of from 10 to 20 or more carbon atoms, which are either saturated or unsaturated. Cocoabutter is a preferred lipid.

[0063] As used herein, the phrase "drying to its original water content" means to restore the article or item in question to within ±10% of its original water content. More preferably, it means to restore the article or item in question to ± 5% of its original water content.

EXAMPLES

Example 1

[0064] Dozens of film formulations were explored in the course of arriving at the present invention. This Example and Example 2 set forth exemplary studies of differences in gloss and gloss stability of four of the formulations tested.

Materials and methods for gloss stability studies:

[0065] The whey-protein-based coatings included WPI (Bipro®, Davisco Foods International, Lesuer, MN, USA) as a film-forming agent. Plasticizers included: sucrose (granulated pure cane sugar, C & H Inc., Crockett, CA, USA), glycerol (USP/FCC, Fisher Scientific Inc., Fair Lawn, NJ, USA), propylene glycol ("PG," USP/FCC, Fisher Scientific Inc., Fair Lawn, NJ, USA) and poly ethylene glycol 400 ("PG-400," NF, Fisher Scientific Inc., Fair Lawn, NJ, USA). Cocoabutter (Blommer Chocolate, Union City, CA, USA) was added to some WPI/plasticizer formulations to aid the coating process, by increasing coating solids content and reducing coating tack marks.

[0066] Heat-denatured 10% WPI solution was used as the base solution. The denatured solution was prepared by heating 10% native WPI solution (w/w) for 30 min in a water bath at 90° C (McHugh and Krochta, J. American Oil Chemist Society, 71(3): 307 – 312 (1994)). The heat-denatured solution was then cooled down to room temperature using an ice bath, and each plasticizer was added at a 1:1 ratio of WPI to plasticizer. For those formulations including cocoabutter, melted cocoabutter was added to the heat denatured WPI solution in the amount of 2 parts cocoabutter to 3 parts denatured WPI. This formulation then was emulsified for 5 minutes using a hand blender (Braun hand blender MR360, Braun Inc., Woburn, MA, USA). After the emulsion was cooled down to room temperature with an ice bath, native WPI was added at a level of 1 part denatured WPI to 1 part native WPI. Each plasticizer was added to the emulsion in the amount of 1 to 1 ratio of the total WPI to plasticizer. The total solids content of the final formulation was 33.42%. Two batch replications of each WPI/plasticizer formulation were made to investigate the effect of formulation batch replications on gloss of the chocolate samples. This formulation batch replication is denoted as formulation replication throughout this paper.

Coating casting and drying onto matte black acrylic plates

[0067] WPI/plasticizer formulations with and without cocoabutter were cast on 4 in x 4 in x 1/8 in thick sheets of matte black acrylic plastic plates (Tap Plastics, Sacramento, Calif., U.S.A.), using a Bird-type applicator (Paul Gardner Co., Pompano Beach, Fla., U.S.A.). Coatings were dried at ambient conditions (22-25°C, 33-45% RH) for 24 h. The resulting dry coating thickness was aimed at 42.4 μm.

Coating procedure and batch preparation for chocolate samples

[0068] For the four formulations containing cocoabutter and differing in plasticizer types, the coating was done with a pan coater (LP16, LMC International, Elmhurst, IL, USA) with a diameter of 16 inches. This coater is a conventional coater used in the confectionery industry. The coating formulation was ladled onto the unglazed milk chocolate covered almonds (10832801, Shade foods Inc., Union City, CA) and evenly distributed by rotating the pan at 72 rpm. The rotation was stopped once the solution was completely applied (about 30 seconds), then the drying process was started. The batches were dried in the pan using cool air (10 - 20°C).

[0069] The drying process consisted of drying one side of the batch, then 180° rotation of the pan to flip the sample batch to the other side, then drying that side. The drying cycle was about 10 - 20 min each side, with about 4 - 6 flips. Hence, the total drying time was in the range of 1.5 to 2 h. Two coatings were applied for each treatment. After each coating application, the process batch was laid out in a room with a temperature range of 15 - 20°C for ~24 h. Two process batch replications were made for each formulation replication. This process batch replication is denoted as the process replication throughout this paper.

[0070] Since the a_w values of the commercial chocolates were in the range of 0.35 to 0.4, we attempted to adjust the a_w of the coated chocolate samples in this study back to within the same range. Thus, after the second coating was applied and the coating was completely dried for ~24 h, the batches were conditioned in constant relative humidity (RH) chambers (Fisher Scientific, Fairlawn, NJ, USA) at RH of 20 % to decrease their a_w from 0.5 to 0.35. RH of the chamber was achieved using saturated salt solution of magnesium chloride (Certified A.C.S., Fisher Scientific Inc., Fair Lawn, NJ, USA) and moisture absorbent sachets (silica gel pillow pack, Desiccare Inc., Santa Fe Springs, CA, USA). Thus, the RH of the chamber was ~ 20%, and the a_w of the chocolate samples equilibrated around 0.35 within 3 to 4 d. Once the a_w of the samples reached 0.35, they were stored in 473 ml mason jars in ambient conditions, and the gloss was measured periodically until it stabilized. The chocolate samples were stored in three different mason jars for each process replication. This was regarded as the storage replication.

Instrumental gloss measurement procedure

(i) MICRO-TRI-GLOSS measurement

[0071] The gloss of the coatings on acrylic plastic plates was measured using a MICRO-TRI-GLOSS meter (BYK Gardner, Silver Spring, Md., U.S.A.). Specular gloss, otherwise

known as the perception of "shininess," is defined as the intensity of light that is specularly reflected from a sample surface compared to the intensity of light that is specularly reflected from a known standard surface at a given angle of incidence (Standard test method for specular gloss. Designation D523. 1995 Annual Book of ASTM Standards. Volume 6.01: Paint-tests for chemical, physical and optical properties; appearance; durability of non-metallic materials. Philadelphia, Pa.: American Society for Testing and Materials, 1995 (hereafter, "ASTM 1995)). Gloss of the coatings was measured at three different angles of incidence, 20°, 60° and 85° from the normal to the coating surface (ASTM 1995). Polished black glass with a refractive index of 1.567 was used as the standard surface (ASTM 1995). A gloss value of greater than 70 when measured at 60° angle of incidence is considered to be high gloss, and a gloss value of smaller than 10 at 60° angle of incidence is considered to be low gloss. An 85° angle of incidence can aid in differentiating low gloss samples, whereas 20° can aid in differentiating high gloss samples. The matte black acrylic casting plates had gloss values of 0.2, 1.7 and 6.1 when measured at the angle of incidence of 20°, 60° and 85°, respectively. These low gloss values indicated that there was no double reflection effect to interfere with the gloss measurements of the coatings.

Tricor gloss meter measurement

[0072] The gloss of coatings on acrylic plastic plates and the gloss of the chocolate samples were measured using a Tricor gloss meter (801A, Tricor Systems Inc., Elgin, IL, USA). The Tricor gloss meter allows measuring of gloss of samples with curved surfaces. Before the gloss of the sample is measured, the instrument is calibrated using a calibration reference plate with gloss value of 274. The gloss of the reference plate when measured using the MICRO-TRI-GLOSS meter was 91.9, 94.8 and 99.9 at 20°, 60° and 85° angles from the normal to the plate surface. For the gloss measurement of the sample, gloss data is extracted from a grey scale image of the sample generated by the instrument. The grey scale image consists of many pixels, and brighter pixels indicate more gloss at that location. In order to quantify gloss of a curved surface, pixels with similar brightness are grouped together, and the average gloss of those pixels is calculated. A group can be specified by the experimenter, and is usually represented as the x% of the brightest pixels above a threshold designated by the experimenter. The threshold value should be set high enough so that the gloss of the sample is the only gloss values taken for the average gloss. In this study, the average gloss of the 5% of the brightest pixels was recorded for each sample, and the threshold value was

designated as 45. Each chocolate sample was measured three times for each storage replication, and this was regarded as the instrumental replication.

Statistical analysis

[0073] Correlation analysis was conducted with Excel® software (Microsoft office 98 Version 8.0 for Apple® Macintosh® Series, Microsoft Corp.) for the two gloss data sets measured by the MICRO-TRI-GLOSS meter and the Tricor gloss meter. Analysis of variance (ANOVA) and Fisher's least significant differences (LSD) ($p < 0.05$) were executed with the SAS software (SAS version 6.12, 1996) on the gloss values for the chocolate samples measured by the Tricor gloss meter.

Example 2

Results and Discussion

Correlation for the two gloss data sets measured by the MICRO-TRI-GLOSS meter and the Tricor gloss meter

[0074] The gloss data sets for WPI coatings with and without cocoabutter on acrylic plastic plates measured by the Tricor gloss meter averaged for 15% brightest pixels were compared to those measured by the MICRO-TRI-GLOSS meter at 20°, 60° and 85° angle of incidence, respectively. The correlation coefficients (r) at different angles of incidence were all significant at $p < 0.001$, indicating that the Tricor gloss meter generates gloss data in correlation to that of the MICRO-TRI-GLOSS, which is a standard gloss measurement (ASTM 1995). The correlation coefficient and the determination of correlation (r^2) increased with increasing angle of incident light source of the MICRO-TRI-GLOSS, which indicated that the Tricor gloss meter is more efficient in differentiating low gloss samples. This finding was also shown by the trend of the data sets. The Tricor gloss meter was able to differentiate samples with similar gloss values from the MICRO-TRI-GLOSS meter for low gloss samples, whereas the MICRO-TRI-GLOSS was more efficient in distinguishing samples of similar values for high gloss samples. The significant r and the high r^2 values gave validity for using the Tricor gloss meter to measure gloss of the curved chocolate surface.

Gloss values for chocolate samples glazed with 4 different WPI/plasticizer formulations

[0075] The variance of results on the gloss values of the 15% brightest pixels for the four WPI/plasticizer coated chocolate samples, as measured by the Tricor gloss meter, was analyzed. The plasticizer treatment factor was a significant source of variation ($p < 0.001$), indicating that different plasticizers significantly affected the resulting coating gloss on the chocolate surface. The formulation replications differed significantly from each other ($p < 0.001$), indicating that the different batches of WPI formulations made in different days affected the gloss of the chocolate samples. This suggests that the difference in the environmental conditions such as temperature and relative humidity of the different days those formulation batches were made and/or applied significantly affected the gloss of the chocolate samples. The process replications which were made on the same day under similar room temperature and RH did not show a significant difference. These results from formulation replications and process replications indicate that environmental conditions such as the relative humidity and the room temperature were important in affecting the resulting gloss on the chocolate surface. Neither the storage replications nor the instrumental replications were a significant source of variation.

[0076] The plasticizer sucrose resulted in the highest gloss, followed by PG, then by PEG 400, and lastly by glycerol. β-lactoglobulin films made with these same plasticizers showed different oxygen permeability properties and different mechanical properties. Among the films investigated, sucrose-plasticized films had the lowest oxygen permeability and were characterized as the stiffest and strongest film in terms of mechanical properties. However, there is no literature on the effect of different plasticizers on the gloss of whey protein or any other films or coatings.

[0077] The difference in the initial average gloss values was not the only different phenomena resulting from different plasticizers. There was a significant difference in the gloss fade rate and the stabilized gloss values. Glycerol-plasticized and PEG 400-plasticized coatings had very low gloss values and that faded away within days. Glycerol- and PEG 400-plasticized coatings stabilized at lower gloss values than the PG- and sucrose-plasticized coatings. The gloss fade of the PG-plasticized coatings occurred over a month period, and the coatings developed visible cracks and flakes during this period. The gloss fade of the sucrose-plasticized coatings occurred over a longer period of time and the gloss stabilized at a higher value compared to the other plasticizers. The gloss fade may have resulted from plasticizer migration into the chocolate. Since sucrose is a non-linear bulky compound, this

may have impeded sucrose migration into the chocolate. Also since chocolate contains sucrose, there existed a smaller gradient from the WPI/plasticizer coating to the chocolate. This may have also affected slower migration of sucrose into the chocolate compared to the other plasticizers.

Example 3

[0078] This Example sets forth the experimental procedures for measuring consumer acceptance of WPI coatings compared to shellac and other coatings.

Materials and Methods

Coating Solutions

Whey Protein Coatings

[0079] The whey protein coatings included WPI (Bipro®, Davisco Foods International, Lesuer, MN, USA) as the film-coating agent and sucrose (Granulated pure cane sugar, C & H Inc., Crockett, CA, USA) as a plasticizer. Cocoabutter (Blommer Chocolate, Union City, CA, USA) was added to produce a WPI-plasticizer-lipid formulation. Cocoabutter was used as the lipid source, because cocoabutter is label-friendly when used on confectioneries. Cocoabutter also has a low melting point and gives small particle size when emulsified with WPI solution, resulting in higher gloss (Trezza, et al., *J. Food Sci.*, **65**(4): 658-662 (2000)).

[0080] There were four WPI treatments: Two without lipid which varied in the native WPI amount, and two with lipid which varied in lipid amount. Table 1 shows the ratio of the constituents in each WPI coating treatment. The sample codes in Table 1 are used throughout the paper. Shellac treatment was used as the reference. The denatured solution was prepared by heating 10% WPI solution (w/w) for 30 minutes in a water bath at 90°C (McHugh, et al., *J. American Oil Chemist Society*, **71**(3): 307-312 (1994). The denatured solution was then cooled down to room temperature (~25°C) in an ice bath for those solutions which did not contain lipid. For lipid-containing treatments, cocoabutter which had been melted was added to the heat-denatured WPI solution, and then emulsified for 5 minutes using a hand blender (Braun hand blender MR360, Braun Inc., Woburn, MA, USA). The emulsion was cooled down to room temperature using an ice bath. The resulting emulsion had a bimodal particle-size distribution, and the mean particle size was approximately 1.7 μm measured by the Malvern Master-sizer (model MS 20, Malvern Instruments Ltd., Malvern, England) recorded as the D(3,2) diameter. The native WPI was added after the solution was cooled down to

room temperature. Sucrose was added to all coating solutions in a 1 to 1 ratio of the total WPI to sucrose.

Table 1.

The ratio (wt. basis) of the constituents in each WPI coating treatment. The sample codes are capitalized and underlined.

	WPI without cocoabutter (Denatured: Native = 1:1) DN11WO	WPI without cocoabutter (Denatured: Native = 1:2) DN12WO	WPI with cocoabutter (DWPI: cocoabutter = 3:2) W32	WPI with cocoabutter (DWPI: cocoabutter = 1:1) W11
Denatured WPI (DWPI)	1	1	1	1
Native WPI (NWPI)	1	2	1	1
Sucrose	2	3	2	2
Cocoabutter	0	0	2/3	1
Water	9	9	9	9

Shellac Coating

[0081] Shellac coating solution was made using 190 proof undenatured ethyl alcohol (ET108, USP, Spectrum Chemical Mfg. Corp., Gardena, CA, USA) as the solvent. Refined shellac powder (Type R-49, Mantrose-Haeuser Co., Attleboro, Mass., USA) was dissolved in the ethanol to form 30% (w/w) solution. Typically, a 25-30% shellac solution is used commercially, with the variation in the strength of the solution depending on the confectionery product being glazed (Minifie, B.W., *Chocolate, Cocoa & Confectionery: Science & Technology*, 2nd Ed., AVI Publishing Company, Inc., Westport, Connecticut, pp. 105-127 (1980a). Propylene glycol (USP/FCC, Fisher Scientific, Fair lawn, NJ, USA) was added in a 1 to 9.3 ratio of propylene glycol to shellac. The mixture was stirred until shellac was completely dissolved.

Gum Coating

[0082] Prior to coating with shellac solution, the chocolate-covered almonds were precoated with gum solution to prevent migration of ethanol into the chocolate. Gum coating solution was prepared by dissolving corn syrup solids (Cantab, Penwest Foods, Richland, WA, USA) into boiling water to make 20% solution. To this solution, tapioca dextrin (K-4484, National Starch and Chemical Co., Bridgewater, NJ, USA) and xantham gum (Keltrol T, Kelco, Division of Merck & Co. Inc., San Diego, CA, USA) were added at a 1 part corn syrup solids to 3.7 part tapioca dextrin and 0.02 part xantham gum. The solution was

thoroughly mixed until the solids were totally dissolved. The total solids of the resulting gum solution was 54% (w/w).

Chocolate-covered Almonds

[0083] Unglazed milk-chocolate-covered almonds were purchased from Shade foods Inc. (10832801, Shade foods Inc., Union City, CA).

Coating Procedure and Batch Preparation

WPI treatments

[0084] For all four WPI coating treatments, the coating was done using a pan coater (LP16, LMC International, Elmhurst, IL, USA) with a diameter of 16 inches. The coating solution was ladled onto the unglazed milk-chocolate-covered almonds and evenly distributed by jogging (rotating) the pan. The jogging process was stopped after the solution was completely applied. The coated batch was then dried using cool air (10-20°C).

[0085] The drying process consisted of drying one side of the batch in the pan, then rotating the pan 180° to flip the batch to the other side for drying. The drying time was 10-20 minutes on each side, with 4-6 flips. Hence, the total drying time was in the range of 1.5 to 2 hours. Three coatings were applied for each batch treatment. After each coating application, the coated batch was laid out in a single layer in a room with a temperature range of 15-20°C for ~24 hours. Since the a_w of the commercial chocolate-covered almonds was in the range of 0.35 to 0.4, we adjusted the a_w of the WPI-coated chocolates in this study back to this same range. Thus, after the third coating was applied and the coating was completely dried for ~24 hours, the coated batch was conditioned in a constant relative humidity (RH) chamber (Fisher Scientific, Fairlawn, NJ, USA) at RH to decrease batch a_w from ~ 0.5 to 0.35. RH of the chamber was achieved using a saturated salt solution of magnesium chloride (Certified A.C.S., Fisher Scientific Inc., Fair Lawn, NJ, USA) and moisture-absorbent sachets (silica gel pillow pack, Desiccare Inc., Santa Fe Springs, CA, USA). Initially only the saturated magnesium chloride solution (RH ≈33%) (Carr and Harris 1949; Rockland 1960) was used. However, a preliminary experiment indicated that the a_w of WPI-coated batch did not equilibrate with the RH of the chamber after a 2 week period. Thus, the RH of the chamber was lowered to 20% RH using moisture absorbent sachets, and the a_w of the WPI-coated chocolate batch then equilibrated to ~ 0.35 within 3 to 4 days. After the a_w of the WPI-coated batch reached 0.35, the coated chocolates were stored in half gallon mason jars in a refrigerator (5-10°C) until they were taken out to be tested by consumers.

Gum solution and shellac treatment

[0086] The coating procedure used for the gum coating solution was the same as that used for the WPI coating treatments. The drying time for the gum coating was also similar to that of the WPI coating treatments. Also, similarly, 3 gum coatings were applied onto the chocolate surface. Normally, 1 to 5 gum coatings are applied to ensure full coverage of the chocolate surface in a commercial polishing step (Thomas 1987).

[0087] After the third gum coating was dried for ~ 24 hours, shellac glaze was applied onto the batch. The coating procedure for the shellac-coated batch was also the same as that used for the WPI coating. The total drying time for the shellac-coated batch was only about 20 minutes with 5 flips, since it took much less time to evaporate ethanol solvent. The shellac-coated batch was then laid out in a single layer in a room with a temperature range of 20-24°C. Then the batch was also conditioned in the RH chamber to lower a_w to ~ 0.35. After the a_w reached 0.35, the shellac-coated chocolates were stored in half gallon mason jars in the refrigerator (5-10°C) until they were taken out to be tested by consumers.

Instrumental gloss measurement procedure

[0088] The gloss of chocolate samples was measured using a Tricor gloss meter (801A, Tricor Systems Inc., Elgin, IL, USA). The Tricor gloss meter measures gloss of samples with curved surfaces. Before the gloss of a sample is measured, the instrument is calibrated using a calibration reference plate with gloss value of 274. The gloss of the reference plate when measured using MICRO-TRI-GLOSS meter (BYK Gardner, Silver Spring, MD, USA) was 91.9, 94.8 and 99.9 at 20°, 60° and 85° angles from the normal to the plate surface, respectively. For the gloss measurement of a sample, gloss data is extracted from a grey-scale image of the sample generated by the Tricor instrument. The grey-scale image consists of many pixels, and brighter pixels indicate more gloss at that location. In order to quantify gloss, pixels with similar brightness are grouped together and the average gloss of those pixels is calculated. A group can be specified by the experimenter and is usually represented as x% of the brightest pixels above a threshold value which is determined by the glossiness of the sample being measured. The threshold value should not be set too high to disregard the values from the glossy area of the sample, and it should not be set too low to take the values from the non glossy part of the sample. In this study, the average gloss of the 5% of the brightest pixels was recorded for each sample, and the threshold value was designated as 45. Each chocolate sample was measured three times, and this was regarded as the instrumental replication.

Example 4

This Example sets forth the consumer acceptance test procedure.

Consumers

[0089] One hundred and eighty consumers (80 male, 100 female) recruited at the Memorial Union of the University of California, Davis, participated in this study. The consumers were screened using a questionnaire. The screening questionnaire consisted of questions involving allergic responses to the samples and ingredients in the coating and frequency of the purchase and consumption of chocolate products. Only the consumers with no allergic responses who purchase and consume chocolate products at least once a month were selected.

Sample Preparation and Presentation

[0090] Samples were taken out from the refrigerator at least 2 hours prior to the start of the first consumer's evaluation, in order to equilibrate to room temperature. Samples were served at room temperature in 2 oz plastic cups (Rykoff-Sexton, Inc., Lisle, IL, USA) labeled with 3-digit random codes generated by the random numbers table (O'Mahony, M., Chi-square. In: Fennema OR, Karel M, Sanderson GW, Tannenbaum SR, Walstra P, Whitaker JR, editors. *Sensory evaluation of food - Statistical methods and procedures*. Marcel Dekkar Inc., New York, New York, p 91-110 (1986a). The presentation order of the samples for each consumer was designed based on the complete set of mutually orthogonal latin squares (MOLS) design (Wakeling, I.N., *Food Quality and Preference*, **6**: 299-308 (1995). The complete set of MOLS design is balanced for all carry-over effects up to and including order t-1, where t is the number of products (Wakeling, I.N., *Food Quality and Preference*, **6**: 299-308 (1995). In this study, 9 complete sets of MOLS were used for the five samples with 180 consumers.

Experimental Protocol

[0091] The screened consumers were asked to fill out Product Attitude Survey I, which consisted of general questions such as, age, gender and occupation. They were also asked if they were on a special diet such as low salt, low fat, low calorie, diabetic, high calorie or no special diet, to assess any correlation of their liking of a specific coating treatment to their special diet.

[0092] Each sample cup contained 4 to 5 pieces of chocolate covered almonds. All five samples, representing the four WPI treatments and the shellac coating, were presented at once in a tray. Consumers were asked to rate the samples in a specified order written on a sticky note placed in the corner of the sample tray. Consumers were asked to rate the samples for

overall degree of liking (DOL) and DOL of taste, DOL of texture, DOL of overall appearance, DOL of surface texture (appearance) and DOL of gloss, all on a nine-point hedonic scale (Peryam, et al., Food Technology, **11**(9), Suppl. 9-14 (1957). The nine-point hedonic scale and corresponding anchoring terms were placed on the table. Consumers were asked to physically place the samples on the scale according to their rating. When the rating was completed for each attribute, the DOL scores were recorded by the experimenters and the samples were placed back into the tray in the order given on the sticky note to be evaluated for the next attribute. This procedure was followed for two reasons: first, to avoid any repetition of the scores without re-evaluating the samples due to the fact that consumers have access to their previous scores and, second, to avoid any mistakes made by untrained consumers when recording the data. Consumers were instructed to taste and swallow the samples for overall DOL, DOL of taste and DOL of texture attributes. Rinsing protocol consisted of one carbonated water (Select, Safeway, Davis, CA, USA) followed by one drinking water (Black Mountain Spring Water, San Carlos, CA, USA). Consumers were strongly advised to rinse in between each sample. Consumers were allowed to retaste the samples, if needed, and were allowed to change the rating of previous samples. For the appearance attributes, consumers were asked to observe the samples visually and rate.

[0093] After the rating session was over, consumers were asked to complete Product Attitude Survey II, which consisted of questions regarding their change in acceptance and in purchase intent had they known given information about shellac glaze. The total session length ranged from 15 to 25 minutes.

<u>Statistical analysis</u>

[0094] Analysis of variance (ANOVA) and Fisher's least significant differences (LSD) ($p<0.05$) were executed with SAS software (SAS version 6.12, 1996) on the hedonic ratings for the chocolate (overall DOL, DOL of taste, texture, overall appearance, surface texture (appearance only) and gloss). Internal preference mapping (a principal component analysis (PCA) of the covariance matrix of consumers by products) was done on the consumer acceptance data using FIZZ software (Biosystèmes; Couternon, France).

Example 5

<u>Results and Discussion</u>

Instrumental gloss values

[0095] The mean instrumental gloss values measured by the Tricor gloss meter (801A, Tricor Systems Inc., Elgin, IL, USA) for the five treatments are shown in Table 2, along with

their standard deviations. The mean gloss values of the WPI treatments ranged from 186 to 239.67. WPI treatments with more cocoabutter exhibited less gloss and WPI treatments with more native WPI showed more gloss. The mean gloss value of the shellac-coated chocolates was within the range of the mean gloss values of the WPI treatments, indicating that the WPI treatments were successful in providing gloss to the chocolate surface comparable to the shellac treatment.

Table 2.

The mean and the standard deviation of the instrumental gloss values for the five treatments measured by the Tricor gloss meter.

The codes for the samples are in Table 1.

	DN11WO	DN12WO	W11	W32	Shellac
Average Gloss Value	234.33	239.67	186.00	200.67	227.67
Standard Deviation of the three replications	8.08	7.09	3.46	8.50	6.03

Consumer acceptance test

[0096] ANOVA of the hedonic ratings for overall DOL ($F = 3.56$, $P < 0.01$), DOL of taste ($F = 4.96$, $p < 0.001$), texture ($F = 6.54$, $p < 0.001$), overall appearance ($F = 45.02$, $p < 0.001$), surface texture (appearance) ($F = 55.09$, $p < 0.001$) and gloss ($F = 25.67$, $p < 0.001$) differed significantly. Mean overall DOL, DOL of taste, texture, overall appearance, surface texture (appearance) and gloss ratings and the least significant differences (Fisher's LSD) of the 5 samples are shown in Table 3.

Table 3.

Sample means for the degree of liking and LSDs for all attributes.

Means with different letters are significantly different ($p < 0.05$). The codes for the samples are in Table 1.

	DN11WO	DN12WO	W11	W32	Shellac
Overall	5.94ab	5.68b	6.14a	6.22a	5.96ab
Taste	5.90bc	5.69c	6.31a	6.18ab	5.83c
Texture	5.46c	5.49c	6.12a	5.91ab	5.59bc
Overall Appearance	4.69c	4.29d	6.28a	5.13b	5.22b
Surface Texture (Appearance)	4.68c	4.31d	6.39a	4.97c	5.61b
Gloss	4.69c	4.46c	6.30a	5.59b	5.31b

[0097] It was found from the instrumental results and the consumer acceptance results that the consumers had higher liking for the samples with less gloss and more smooth appearance. They not only liked these samples rated by appearance, but they also preferred these samples when rated by the taste and texture attributes. This trend was also shown for overall DOL. The mean hedonic ratings for all 6 attributes of the W11 treatment were above 6 (= slightly like) on a 9-point hedonic scale. For the W32 treatment, the mean hedonic ratings were in the range of 4.97 to 6.22. This treatment was liked the most for overall DOL, but for specific attributes, it ranked second or third. For shellac-coated treatment, the mean hedonic ratings were in the range of 5.22 to 5.96, where 5 equals to neither like nor dislike on the 9-point hedonic scale. For most of the attributes, the W11 and W32 treatments were liked the most, followed by the shellac-coated treatment, and lastly by the DN11WO and DN12WO treatments. The W11 treatment ranked first, followed by shellac treatment, for DOL of overall appearance and surface texture (appearance) attributes.

Product Attitude Survey II

[0098] Consumers completed the Product Attitude Survey II after they had completed the rating session. The first question in this survey was an open-ended question: "What things do you associate with shellac?" This question was followed by a brief description of shellac uses including edible shellac. There were five categorical questions which are listed in Table 4. Figures 1 to 5 are the plots for the number of consumers for each category of those questions. The data reveal that the majority of the consumers were not familiar with the term "shellac", and so the majority of them were neutral in their liking of those products containing shellac. And this resulted in "no change" in their purchase intent for those products containing shellac. However, the majority of the consumers expressed "strong dislike" or "dislike" of those products associated with beetle exudate, thus their purchase intent was decreased. These questions were analyzed by the chi-square test. Chi-square is used to test hypotheses about frequency of occurrence in two or more categories. In general, chi-square is given by the following formula (O'Mahony, M., Chi-square. In: Fennema OR, Karel M, Sanderson GW, Tannenbaum SR, Walstra P, Whitaker JR, editors. *Sensory evaluation of food - Statistical methods and procedures*. Marcel Dekkar Inc., New York, New York, p 91-110 (1986a):

$$\text{chi-square} = \sum\left[\frac{(O-E)^2}{E}\right]$$

where, O = observed frequency and E = expected frequency if the null hypothesis were true. The calculated chi-squares were compared to the critical chi-square values given in a table according to their degrees of freedom (O'Mahony, M., Statistical tables, Table G.7. In: Fennema OR, Karel M, Sanderson GW, Tannenbaum SR, Walstra P, Whitaker JR, editors. *Sensory evaluation of food - Statistical methods and procedures.* Marcel Dekkar Inc., New York, New York, p 415 (1986b).

Table 4.

Questions and categories presented in Product Attitude Survey II

Questions	Calculated chi-squres	Degrees of Freedom (df)	Significance level
Q1: Did you know that some foods contain shellac? (2 categories)	55.56	1	$p < 0.001$
Q2: How would you feel about food that has shellac as an ingredient? (5 categories)	182.39	4	$p < 0.001$
Q3: How would knowing a food contained shellac affect your purchasing intent? (3 categories)	74.63	2	$p < 0.001$
Q4: How would you feel about beetle exudate associated with food? (5 categories)	103.39	4	$p < 0.001$
Q5: How would knowing a food contained beetle exudate affect your purchasing intent? (3 categories)	89.2	2	$p < 0.001$

[0099] For each question presented in Table 4, chi-square was calculated. The calculated chi-square values, the degrees of freedom for each question, and the corresponding significance level are also shown in Table 4. For all the five categorical questions, there was a significant difference in the distribution of the number of consumers who chose one category over the others.

Example 6

Conclusion of the studies reported in Examples 3-5.

[0100] The results strongly suggested that there is a high potential for the WPI formulations studied to be used as a chocolate glaze alternative to shellac glaze.

[0101] Different constituents in the coating formulation, such as the amount of lipid added to the WPI formulation and the level of native vs. heat-denatured WPI added, can significantly affect the appearance, taste and texture of the coating. Heat-denatured WPI produces films that are stronger, stiffer and more extendible compared to films from native WPI (Pérez-Gago and Krochta, 1999). However, the influence on the appearance, taste and texture of the WPI-coated chocolate product and how these affect consumer acceptance can only be evaluated by sensory methods. The consumer acceptance test measures the acceptability or liking for a food. Thus, the test provides a means to estimate the acceptance of the product based on its sensory properties (Resurreccion, A.V.A, Sensory test methods.

In: Bloom R., ed, *Consumer sensory testing for Product Development*, Aspen publication, Aspen publisher inc., p 9-42 (1998).

Example 7

[0102] This study, and the ones below, concern the effect of WPI coatings on nuts, and especially peanuts.

Raw Materials

[0103] The variety of peanuts used for the studies herein was "medium runner". The peanuts contained 48-52% lipid, 22-30% protein, 3-5% sugar and less than 2% moisture ($a_w \approx$ 0.25).

[0104] The whey protein coatings included WPI (Bipro®, Davisco Foods International, Lesuer, MN, USA), glycerol (USP/FCC, Fisher Scientific Inc., Fair Lawn, NJ, USA) as a plasticizer, lecithin (Centrolene® A, Central Soya Company, Fort Wayne, IN, USA) as a surfactant and methyl paraben (NF/FCC, Fisher Scientific Inc., Fair Lawn, NJ, USA) as an antimicrobial agent. Vitamin E (Nature's Life, Gardengrove, CA, USA) was added to some of the coating formulations to test its antioxidant properties.

Sample Treatments and Storage conditions

[0105] Both native and heat-denatured WPI were included in the study, because they produce films with different solubility, tensile strength and oxygen-barrier properties (Pérez-Gago et al., *J. Food Sci.*, 64(6):1034-1037 (1999); Pérez-Gago and Krochta, *J. Agric. Food Chem.*, 49(2):996-1002 (2001)). There were six sample treatments: 1) heat-denatured WPI without vitamin E, 2) heat-denatured WPI with vitamin E, 3) native WPI without vitamin E, 4) native WPI with vitamin E, 5) control (water + plasticizer + surfactant + antimicrobial agent), and 6) reference (untreated peanuts). All coating solutions contained 10% WPI (w/w). The denatured solution was prepared by heating the 10% WPI solution (w/w) for 30 minutes in a water bath at 90°C (McHugh and Krochta, *J. Agric. Food Chem.*, 42:841-845 (1994)). The denatured solution was then cooled down to room temperature (~25°C) in an ice bath. Glycerol was added to all coating solutions at a 1 to 1 ratio of WPI to glycerol. Lecithin and methyl paraben were added to all coating solutions at 0.05% and 0.1% of the coating solution (w/w), respectively. When vitamin E was added, it was at 0.5% of the coating solution (w/w). The same amount of ingredient(s) was added to water (Arrowhead Mountain Spring Water Company, Brea, CA, USA) to make the control. WPI-vitamin E emulsions were made using a Microfluidizer homogenizer (HC 5000, Microfluidics

International Corp., Newbury, MA, USA). The hot liquid was passed through the homogenizer 6 times using a homogenizing pressure of 6000 psig. The resulting emulsion had a normal particle-size distribution and the mean particle size was approximately 0.6 μm. After all the ingredients were mixed, the solution was strained with 2 layers of cheese cloth and stored for 1 to 3 days at a refrigeration temperature (5 – 10°C) until the coating process took place.

[0106] A commercial coater (Labcoater II system, O'Hara Manufacturing, LTD., Toronto, Canada) was used to coat the peanuts with WPI solutions and control treatment. This coater is a simultaneous spray-jog-dry type of coater which is mainly used to coat pharmaceuticals and nutritional supplements. For our peanut coating, we separated the spray phase and the dry phase of the process.

[0107] For the spray phase, the conditions were the air inlet temperature, 30°C; air exhaust temperature, 15 to 22°C; pan rotation rate, 12 to 18 revolution/min; air flow, 200 cfm. For the dry phase, the conditions were air inlet temperature, 65°C; air exhaust temperature, 19 to 49°C; pan rotation rate, 1 revolution/min; air flow, 750 cfm. The total amount of peanuts coated was 10 Kg. The amount of coating solution applied was aimed at a 5% weight gain of the peanuts after the coating was completely dried. The spray rate was set at 300 g/min per gun, and the actual spray rate was approximately 580 g/min for two guns. The spray phase took approximately 5 min. The duration of the spray phase was calculated according to the spray rate measured just before each spray phase. The drying phase lasted approximately 30 min, and then the peanuts were cooled down to room temperature (~ 25°C) before they were taken out of the pan. Close visual observation of the coated peanuts revealed smooth, glossy coatings without cracks or holes.

[0108] After the coating solution was applied onto the samples and dried, the peanut samples were laid out at room temperature for about 24 hours prior to packaging them into oxygen-barrier bags. They were then held at – 24°C until they were taken out of the freezer to be stored at various storage conditions for headspace GC analysis.

[0109] Peanut samples weighing 180g were placed into wide-mouth 2-quart mason jars (Ball®, Alltrista Corp., Muncle, IN, USA) to be stored at ambient conditions (T $\approx$25°C, RH $\approx$35%). The a_w values of the coated and the control peanuts were adjusted to the range 0.29 - 0.38 using moisture absorbent sachets (silica gel pillow pack, Desiccare Inc., Santa Fe Springs, CA, USA). The number of moisture absorbent sachets added into the mason jars was calculated based on the initial a_w of the coated and the control peanuts and the capacity of the moisture absorbent sachets to absorb a certain amount of water. The a_w of the peanuts

were used to calculate the amount of moisture need to be absorbed in order to achieve the a_w of the reference sample. The a_w of the reference was in the range 0.25 - 0.3. The samples were stored for up to 68 weeks.

Headspace Gas Chromatography Analysis

[0110] Lipid oxidation was evaluated by measuring the hexanal content of the peanut samples by static headspace gas chromatography (GC) (Perkin-Elmer autosystem with HS-40 autosampler, Norwalk, CT). The GC analysis used a capillary DB-1701 column (30 m (l) x 0.32 mm (I.D.), 1mm thickness, J & W, Folsom, CA); HS sampler temperature, 60°C; oven temperature, 65°C; injector temperature, 180°C; detector temperature, 200°C. 5g of peanut samples were ground for 8 seconds using a grinder (Braun coffee bean grinder KSM2(4), Braun Inc., Woburn, MA, USA). Duplicate 0.5g of ground peanut samples were placed into 22 mL headspace sample vials, which were immediately sealed with silicone rubber teflon caps. The vials were then inserted into the headspace sampler at 60°C for 15 minutes and pressurized with carrier gas (He) for 30 seconds. An aliquot of gas phase was injected directly into the GC through the stationary injection needle. The hexanal content of the samples was measured at storage times of 0, 33, 46, 53, 56, 60, 64, 68 weeks.

Example 8

RESULTS AND DISCUSSION

[0111] Results from the analysis of variance (ANOVA) (SAS 6.12, SAS institute Inc., 1996) of the extent of oxidation determined by hexanal level I are shown in Table 5.

Table 5.

Analysis of variance on the hexanal level measured by static headspace gas chromatography for peanut samples. F-ratios are shown for the sources of variations.

Source	**Degrees of freedom**	**F-ratio**
Sample treatment	5	3108.50***
Storage time	7	1485.31***
Experimental replication	1	1.14 NS
Instrumental replication	1	0.42 NS

*** indicates significance at $p < 0.001$. NS indicates no significant difference.

[0112] The coating treatments and storage days and storage temperatures were significant sources of variations ($p < 0.001$). These results were expected since the coating treatments and storage days should have significantly influenced the extent of oxidation of the peanut samples. The experimental replications were two separate jars with the same coating treatment. The instrumental replications were two separate GC vials of the same ground peanut sample. The experimental replications and the instrumental replications were not significant sources of variation.

[0113] The six coating treatments differed significantly in hexanal level. Means and least significant differences (LSDs) for the treatments are presented in Table 6. The LSD results show the characteristics of the different treatments averaged across storage time, experimental replication and instrumental replication. From these results, it can be seen that the untreated peanuts had the highest hexanal level which was significantly different from all the other treatments. Of the coated treatments, native WPI with Vit. E treatment showed the highest extent of oxidation followed by heat-denatured WPI with Vit. E and native WPI without Vit. E. The control treatment showed no significant difference when compared to heat-denatured WPI with Vit. E and native WPI without Vit. E treatments. Heat-denatured WPI without Vit. E treatment had the least oxidation occurring exhibited by the hexanal level being the smallest.

Table 6.

Effect of peanut coating formulations on the extent of lipid oxidation determined by the area under the peak of hexanal. Means with different superscripts are significantly different when analyzed by Fisher's Least Significant Difference ($p < 0.05$).

Peanut coating formulation	Means
Untreated	925.68[a]
Native WPI with Vit. E[1]	276.31[b]
Heat-denatured WPI with Vit. E[1]	213.45[c]
Native WPI without Vit. E[1]	208.24[c]
Control[2]	203.41[c]
Heat-denatured WPI without Vit. E[1]	139.45[d]

[1] Vit. E stands for vitamin E.
[2] Control: glycerol + lecithin + methyl paraben + water

[0114] The nature of the lipid substrates and the nature of the system where Vit. E is added have a significant impact on Vit. E's potential to be an antioxidant or a prooxidant. The literature reports Vit. E levels where it can be an antioxidant or a prooxidant for oils and model emulsion solution systems (Frankel et al., *J. Agric. Food Chem.*, 7:438-441 (1959); Huang et al., *J. Agric. Food Chem.*, 42:2108-2114 (1994); Huang et al., *J. Agric. Food Chem.*, 43:2345-2350 (1995)). However, there are no reported levels of Vit. E in coating systems where it may act as an antioxidant or a prooxidant. And the results in this study indicated that the Vit. E level used in this study was actually in the prooxidant range.

[0115] Plotting of the hexanal level versus storage time showed that the untreated peanut samples went through the initiation and the propagation periods of lipid oxidation, whereas the WPI-treated peanuts and the control peanuts were still at the initiation period.

Example 9

[0116] The results from this study indicated that the heat-denatured WPI without Vitamin E treatment had the least oxidation when stored in ambient conditions. The control treatment without the film-forming WPI also showed significantly less oxidation when compared to the untreated. This may be due to the fact that the control solution when poured onto the peanuts

caused the peanut surface pores to collapse resulting in a denser surface which is less permeable to oxygen.

Example 10

Preparation of water-based coating formulations:

[0117] The whey protein films and coatings included whey protein isolate (WPI) (Bipro®, Davisco Foods International, Lesuer, MN, USA) and sucrose (Granulated pure cane sugar, C & H Inc., Crockett, CA, USA) as a plasticizer for studying gloss and coating of chocolate. Glycerol as the plasticizer and lecithin surfactant were added for studying surface energy of the coating solution and of peanuts, related to the coating of the peanuts.

[0118] The denatured solution was prepared by heating the 10% WPI solution (w/w) for 30 minutes in a water bath at 90°C (McHugh and Krochta 1994). The denatured solution was then cooled down to room temperature (~25 °C) in an ice bath. Sucrose was added to coating solutions in a variety of ratios of the total WPI to sucrose for studying gloss and the coating of chocolate. Glycerol and lecithin were added in a variety of ratios for studying surface energy of the coating solution and of peanuts, related to the coating of the peanuts.

Example 11

Application of the water-based coating formulation to chocolate-coated almonds:

[0119] Five different WPI/sucrose systems were compared to determine which provided the most gloss and which was most durable. The five systems studied had WPI:sucrose ratios of 2:1, 1:1, 1:3, 1:6, and 1:8.

[0120] The specular reflection of films made from the WPI solutions was measured using a Micro-Tri-Gloss meter (ASTM D523-89). To test durability of WPI/sucrose coatings, a single layer of each formulation was applied to chocolate-covered almonds, and gloss measurements were taken with a Tricor Gloss Analysis System model 801. Durability of coatings was tested using a friabilitor following a modified version of ASTM method D441-86. Durability of coatings was correlated to the mechanical properties of stand-alone WPI/sucrose films made with the same ratios.

[0121] For all samples, the coating procedure was done with a pan coater with a diameter of 15 inches at UC Davis. This coater is a conventional coater used in the confectionery industry. The solution was ladled onto samples in the pan coater. The coating solution was applied onto the milk chocolate covered almonds (10832801, Shade Foods Inc., Union City, CA) and evenly distributed by rotating the pan.

[0122] The results indicated that increasing sucrose levels to a WPI:sucrose ratio of 1:3 increased the gloss of WPI films and coatings. Beyond this level, sucrose crystallizes out. This ratio of protein to plasticizer also was found to make the most durable coating and also made the toughest films. With this improved durability, WPI/sucrose coatings are less likely to crack, thereby providing better protection to confectionery products against oxidative rancidity.

Example 12

Application of the water-based coating formulation to peanuts:

[0123] Whey protein films have been shown to be excellent barriers to oxygen. Thus, they can be used as coatings on oxygen-sensitive foods like peanuts to reduce oxidative rancidity. However, adhesion of hydrophilic whey protein coatings to hydrophobic foods such as peanuts is inherently poor due to differences in the chemical nature of the two surfaces.

[0124] To improve the adhesion of whey protein coating on peanuts, we aimed at two mechanisms of adhesion, adsorption and mechanical interlocking. The objectives were to increase the surface energy of peanuts by modifying the peanut surface by surfactant solution treatment and by mechanical roughening.

[0125] Peanuts were treated with aqueous lecithin solution at concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0% (w/w). Surface energies of peanuts were measured and compared before and after treatment. Peanuts were also tumbled together with rock salt in a coating pan for 10, 20, 30, 40 minutes to increase the surface roughness and thus increase the surface energy of peanuts. Surface energy measurement was accomplished by applying a series of test liquids with surface energies in the range of 32 to 70 dynes/cm.

[0126] Blanched, dry-roasted peanuts have a surface energy of 37 dynes/cm. Surface energy of peanuts treated with lecithin solution having a concentration higher than 0.4% was increased to above 70 dynes/cm, by adsorption of lecithin to the peanut surface. Tumbling of peanuts together with rock salt in a coating pan for 30 minutes increased the surface energy of peanuts to above 56 dynes/cm due to increased peanut surface roughness.

[0127] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims. All references cited herein, including journal articles, books, and abstracts, published or corresponding U.S. or foreign patent

applications, issued U.S. or foreign patents, and any other references, are incorporated by reference herein, including all data, tables, figures, and text presented in the cited references.